



Oxford Cambridge and RSA

Tuesday 13 October 2020 – Morning

AS Level Chemistry A

H032/02 Depth in chemistry

Time allowed: 1 hour 30 minutes



You must have:

- the Data Sheet for Chemistry A

You can use:

- a scientific or graphical calculator
- an HB pencil



Please write clearly in black ink. **Do not write in the barcodes.**

Centre number

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Candidate number

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First name(s)

Last name

StemUp Model Solution

INSTRUCTIONS

- Use black ink. You can use an HB pencil, but only for graphs and diagrams.
- Write your answer to each question in the space provided. If you need extra space use the lined pages at the end of this booklet. The question numbers must be clearly shown.
- Answer **all** the questions.
- Where appropriate, your answer should be supported with working. Marks might be given for using a correct method, even if your answer is wrong.

INFORMATION

- The total mark for this paper is **70**.
- The marks for each question are shown in brackets [].
- Quality of extended response will be assessed in questions marked with an asterisk (*).
- This document has **16** pages.

ADVICE

- Read each question carefully before you start your answer.

Answer **all** the questions.

1 This question is about nickel and its compounds.

(a) Nickel reacts with dilute hydrochloric acid in a redox reaction.



Explain, in terms of the number of electrons transferred, whether nickel is oxidised or reduced.

Nickel is oxidised, because each Ni atom loses (donates) two electrons: $\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$.

[1]

(b) A student completely reacts 0.192 g of nickel with $0.150 \text{ mol dm}^{-3}$ HCl(aq).

(i) Calculate the minimum volume, in cm^3 , of $0.150 \text{ mol dm}^{-3}$ HCl(aq) that the student needs for the reaction.

Give your answer to **3** significant figures.

$$n(\text{Ni}) = 0.192 \div 58.7 = 3.27 \times 10^{-3} \text{ mol}$$

$$n(\text{HCl}) = 2 \times n(\text{Ni}) = 2 \times 3.27 \times 10^{-3} = 6.54 \times 10^{-3} \text{ mol}$$

$$\text{volume} = (6.54 \times 10^{-3} \div 0.150) \times 1000 = 43.6 \text{ cm}^3$$

minimum volume of HCl(aq) = ... **43.6** cm^3 [3]

(ii) Calculate the volume of $\text{H}_2\text{(g)}$, in cm^3 , that would be produced at RTP.

$$V(\text{H}_2) = n(\text{H}_2) \times 24000 = 3.27 \times 10^{-3} \times 24000 = 78.5 \text{ cm}^3$$

volume of $\text{H}_2\text{(g)}$ = ... **78.5** cm^3 [1]

(iii) The student repeats the experiment with 0.192 g of magnesium instead of nickel, using the same volume of $0.150 \text{ mol dm}^{-3}$ HCl(aq) as in (b)(i).

State and explain whether the volume of $\text{H}_2\text{(g)}$ produced would be greater than, smaller than, or the same as, the value you have calculated in (b)(ii).

The volume of H_2 is the same (78.5 cm^3).

$0.192 \text{ g Mg} = 0.192 \div 24.3 = 7.90 \times 10^{-3} \text{ mol}$, so Mg is in excess: HCl

is the limiting reagent and the volume of H_2 depends only on the amount

of HCl, which is unchanged.

[2]

(c)* A student is provided with samples of three nickel compounds.

One sample is nickel(II) bromide, another is nickel(II) sulfate and the third is nickel(II) carbonate. The student doesn't know which sample is which.

Describe the tests that the student could carry out to identify the anion (negative ion) in each sample, and write equations for any reactions. [6]

Do the tests in this order on a separate fresh sample of each solid (dissolved in water where needed): carbonate test, then sulfate test, then bromide test, so that no false positives form (BaCO_3 and Ag_2CO_3 , Ag_2SO_4 could also precipitate).

1. Carbonate: add dilute nitric acid, $\text{HNO}_3(\text{aq})$, to each sample. Only nickel(II) carbonate fizzes (effervescence): CO_2 gas is given off, which turns limewater milky. $2\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$, or $\text{NiCO}_3(\text{s}) + 2\text{HNO}_3(\text{aq}) \rightarrow \text{Ni}(\text{NO}_3)_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$.

2. Sulfate: to solutions of the other two samples add barium nitrate solution, $\text{Ba}(\text{NO}_3)_2(\text{aq})$. Nickel(II) sulfate gives a white precipitate of BaSO_4 : $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$.

3. Bromide: to a solution of the remaining sample add silver nitrate solution, $\text{AgNO}_3(\text{aq})$. Nickel(II) bromide gives a cream precipitate of AgBr : $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$. The cream precipitate is insoluble in dilute $\text{NH}_3(\text{aq})$ but soluble in concentrated $\text{NH}_3(\text{aq})$, confirming bromide.

Additional answer space if required

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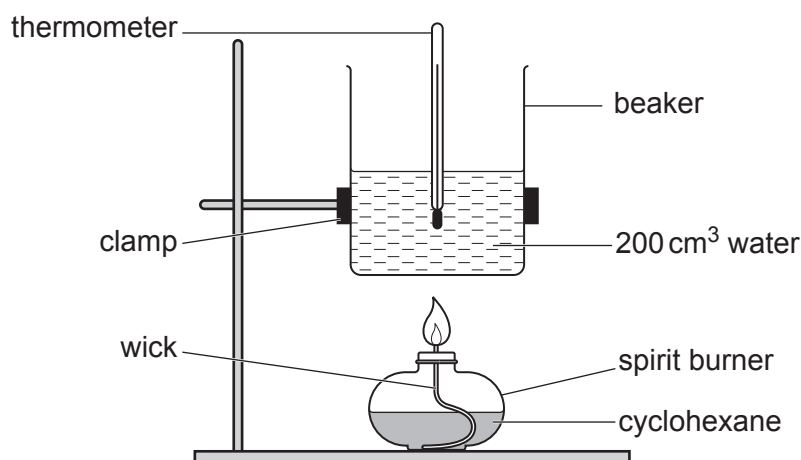
2 Enthalpy changes of combustion can be determined directly by experiment.

(a) Explain the term **enthalpy change of combustion**, $\Delta_c H$.

The enthalpy change when 1 mole of a substance is burned completely in excess oxygen (under standard conditions, 100 kPa and 298 K).

[2]

(b) A student carries out an experiment to determine the enthalpy change of combustion of cyclohexane, C_6H_{12} , using the apparatus shown in the diagram.



In the experiment, 0.525 g of cyclohexane are burnt, and the temperature of the 200 cm³ of water changes from 21.0 °C to 41.0 °C.

Calculate the enthalpy change of combustion, $\Delta_c H$, of cyclohexane in kJ mol⁻¹.

Give your answer to 3 significant figures.

$$\text{energy released, } q = mc\Delta T = 200 \times 4.18 \times 20.0 = 16720 \text{ J} = 16.72 \text{ kJ}$$

$$n(C_6H_{12}) = 0.525 \div 84.0 = 0.00625 \text{ mol}$$

$$\text{energy per mole} = 16.72 \div 0.00625 = 2675.2 \text{ kJ mol}^{-1}$$

$$\text{exothermic, so } \Delta_c H = -2675.2 = -2680 \text{ kJ mol}^{-1} \text{ (3 s.f.)}$$

$$\Delta_c H = \dots\dots\dots -2680 \dots\dots\dots \text{ kJ mol}^{-1} \text{ [4]}$$

- (c) The student finds that their experimental value for $\Delta_c H$ is less exothermic than the value in a data book.

The student evaluates the experimental results.

- (i) The uncertainty in each thermometer reading is $\pm 0.5^\circ\text{C}$ and the uncertainty in the measured volume of water is $\pm 2\text{ cm}^3$.

Determine whether the temperature **change** or the measured volume of water has the greater percentage uncertainty.

$$\Delta T \text{ uncertainty} = 2 \times 0.5 = \pm 1^\circ\text{C}; \% = 1 \div 20.0 \times 100 = 5\%$$

$$\text{volume: } \% = 2 \div 200 \times 100 = 1\%$$

So the temperature change has the greater percentage uncertainty.

[2]

- (ii) Suggest **two** reasons, apart from measurement uncertainties, why the experimental value for $\Delta_c H$ is less exothermic than the data book value.

Reason 1 *Heat is lost to the surroundings (not all of the heat released goes into the water).*

Reason 2 *Incomplete combustion of the cyclohexane (not all of the fuel burns completely).*

[2]

- (iii) In the experiment the water in the beaker was heated for 5 minutes. The student thought that the experiment could be improved by heating the water for 10 minutes.

Explain whether the accuracy in the student's calculated value for $\Delta_c H$ may or may not be improved by heating for longer.

Accuracy may not improve. Heating for longer gives a larger temperature change and a larger mass of fuel burnt, so a smaller % uncertainty (more accurate),

BUT more heat is lost to the surroundings over the longer time, making it less accurate, and this may outweigh the smaller % uncertainty.

[2]

3 This question is about some elements in Period 4 of the periodic table.

(a) The table shows the melting point and electrical conductivity of two elements in Period 4.

Element	Melting Point/°C	Electrical conductivity
Calcium	842	Good
Bromine	-7	Poor

Use your knowledge of structure and bonding to explain the properties in the table.

Calcium has a giant metallic lattice (metallic bonding); Ca^{2+} ions held by strong electrostatic attraction to delocalised electrons.

Bromine is simple molecular (simple covalent), Br_2 molecules held together by weak induced dipole-dipole interactions (London forces).

Conductivity: in Ca the delocalised electrons are mobile and can move to carry charge, so Ca conducts well. In Br_2 there are no mobile charge carriers (electrons are not mobile), so it conducts poorly.

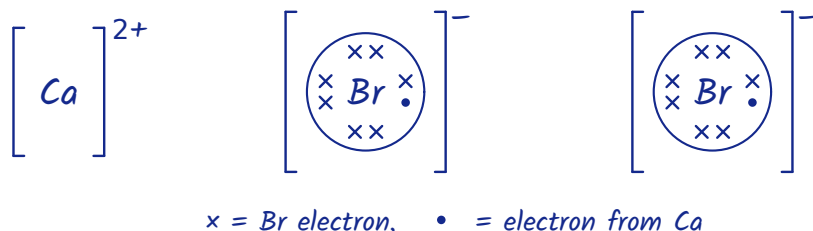
Melting point: metallic bonds are strong and need a large amount of energy to break, so Ca has a high melting point; London forces are weak and need little energy to overcome, so Br_2 has a low melting point.

[5]

(b) Calcium reacts with bromine to form calcium bromide, CaBr_2 .

(i) Draw a 'dot-and-cross' diagram to show the bonding in CaBr_2 .

Show **outer** electrons only.



[2]

(ii) The reaction of barium with bromine is more vigorous than the reaction of calcium with bromine.

Explain why.

*Ba has a greater atomic radius than Ca (more shells) and more shielding.
 So the nuclear attraction on the outer electrons is less in Ba; the
 increased distance and shielding outweigh the increased nuclear charge.
 So the ionisation energy of Ba is less; it is easier to remove the outer
 electrons from Ba, so Ba reacts more vigorously.*

[3]

- (c) The Period 4 element selenium is in the same group of the periodic table as oxygen.

Selenium and oxygen both form compounds with hydrogen with the formulae H_2Se and H_2O respectively.

- (i) H_2Se can be prepared by reacting aluminium selenide, Al_2Se_3 , with water. Aluminium hydroxide and hydrogen selenide are formed.

Write the equation for this reaction.



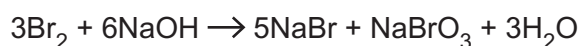
- (ii) The boiling points of H_2O and H_2Se are shown below.

Compound	Boiling point/ $^{\circ}\text{C}$
H_2O	100
H_2Se	-41

Explain why H_2O has a higher boiling point than H_2Se .

H_2O has hydrogen bonds between molecules.
 H_2Se has (only) induced dipole-dipole interactions (London forces) and permanent dipole-dipole interactions, which are weaker.
 Hydrogen bonds are stronger, so more energy is needed to overcome them. [3]

- (d) Bromine reacts with concentrated sodium hydroxide at 50°C as in the equation below.



- (i) Write the systematic name for NaBrO_3 .

sodium bromate(V) [1]

- (ii) This reaction is an example of disproportionation.

Use oxidation numbers to explain why. Include the meaning of the term **disproportionation**.

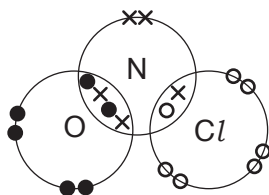
Disproportionation: the same element is both oxidised and reduced.
 Br is oxidised: oxidation number 0 in Br_2 increases to +5 in NaBrO_3 .
 Br is reduced: oxidation number 0 in Br_2 decreases to -1 in NaBr .
 [3]

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- 4 Nitrosyl chloride, NOCl , is used in the industrial manufacture of nylon.

(a) The 'dot-and-cross' diagram for nitrosyl chloride is shown below.



Predict the $\text{O}=\text{N}-\text{Cl}$ bond angle and explain why NOCl has this bond angle.

Bond angle *117° (in the range 112° to 120°)*

Explanation *Around N there is a double bond, a single*

bond and one lone pair (2 bonding regions and 1 lone pair).

The electron pairs repel and get as far apart as possible; the lone pair repels

more than bonding pairs, so the angle is slightly less than 120°.

[3]

- (b) Nitrosyl chloride, NOCl , dissociates into nitrogen monoxide and chlorine as in the equilibrium below.



Nitrosyl chloride is added to a container, which is then sealed.

The container is heated to 400°C , and equilibrium is allowed to be reached.

- (i) Write the expression for the equilibrium constant, K_c , for this equilibrium.

$$K_c = \frac{[\text{NO}(\text{g})]^2 [\text{Cl}_2(\text{g})]}{[\text{NOCl}(\text{g})]^2}$$

[1]

- (ii) In the equilibrium mixture at 400°C , the equilibrium concentration of $\text{Cl}_2(\text{g})$ is found to be 0.17 mol dm^{-3} .

The student calculates that the equilibrium concentration of $\text{NO}(\text{g})$ is 0.34 mol dm^{-3} .

Explain how the student obtained this value for $[\text{NO}(\text{g})]$.

From the equation, 2 mol NO form for every 1 mol Cl_2 ; the ratio NO :

Cl_2 is 2 : 1, so $[\text{NO}] = 2 \times 0.17 = 0.34 \text{ mol dm}^{-3}$.

[1]

- (iii) At 400 °C, $K_c = 0.015 \text{ mol dm}^{-3}$.

Calculate the equilibrium concentration of NOCl(g) at 400 °C.

$$[\text{NOCl}]^2 = \frac{[\text{NO}]^2 [\text{Cl}_2]}{K_c} = \frac{0.34^2 \times 0.17}{0.015} = 1.31$$

$$[\text{NOCl}] = \sqrt{1.31} = 1.14 = 1.1 \text{ mol dm}^{-3}$$

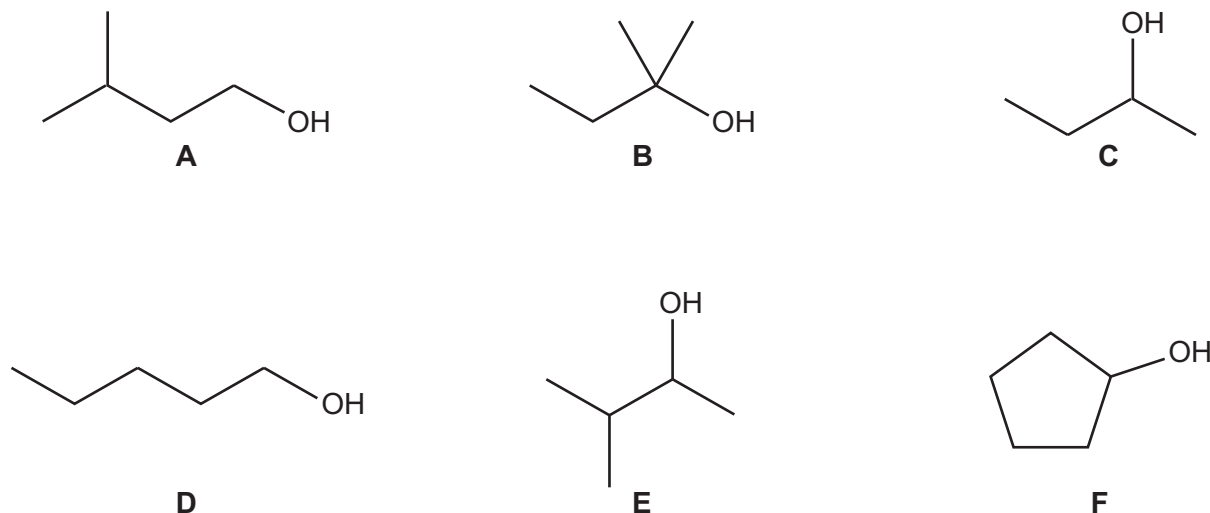
equilibrium concentration of NOCl(g) = ...1.1..... mol dm^{-3} [2]

- (iv) The temperature of the equilibrium mixture is increased above 400 °C while keeping the pressure constant.

State and explain the effect on the equilibrium concentration of nitrogen monoxide, NO(g) , with these new conditions.

The forward reaction is endothermic ($\Delta H = +77.0 \text{ kJ mol}^{-1}$), so as T increases the equilibrium position shifts to the right (in the endothermic direction).
So the equilibrium concentration of NO increases. [2]

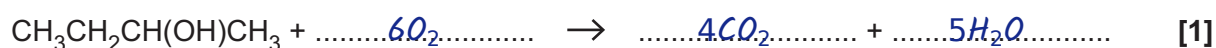
5 This question is about the alcohols **A–F** shown below.



(a) Which of the alcohols **A–F** are secondary alcohols?

C, E and F [2]

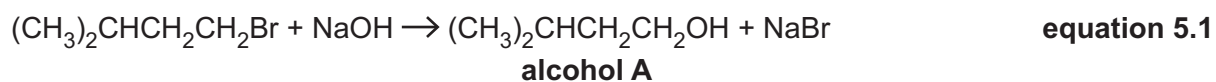
(b) Complete a balanced equation for the complete combustion of alcohol **C**.



(c) What is the systematic name of alcohol **B**?

2-methylbutan-2-ol [1]

(d) Alcohol **A** can be prepared by the alkaline hydrolysis of the bromoalkane, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$. The hydrolysis with aqueous NaOH is shown in **equation 5.1**.



A student gently heats a mixture of $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$ and NaOH(aq) for 25 minutes.

(i) Calculate the atom economy for the preparation of alcohol **A** in **equation 5.1**.

$M_r((\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH}) = 88.0; \quad M_r(\text{NaBr}) = 102.9$

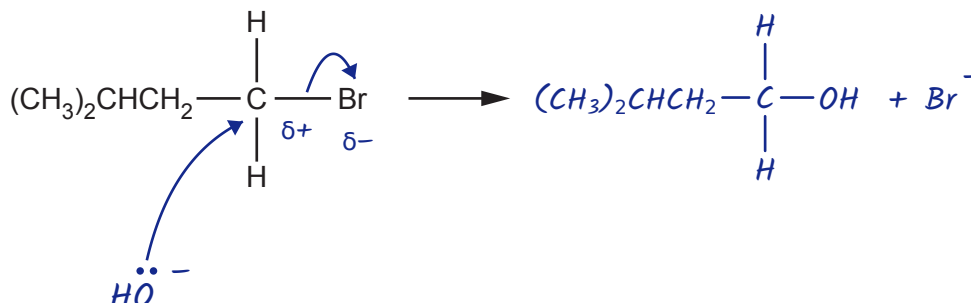
$\text{atom economy} = 88.0 \div (88.0 + 102.9) \times 100$

$= 88.0 \div 190.9 \times 100 = 46.1\%$

atom economy = ... *46.1* % [2]

- (ii) Outline the mechanism for the alkaline hydrolysis of $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$. The structure of $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$ has been provided.

Show curly arrows, relevant lone pairs and dipoles, and the products.



[3]

- (iii) Name this type of mechanism.

nucleophilic substitution

[1]

- (e) The student decides to prepare alcohol **A** using the same method as in (d) but using the chloroalkane $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Cl}$ instead of the bromoalkane, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$.

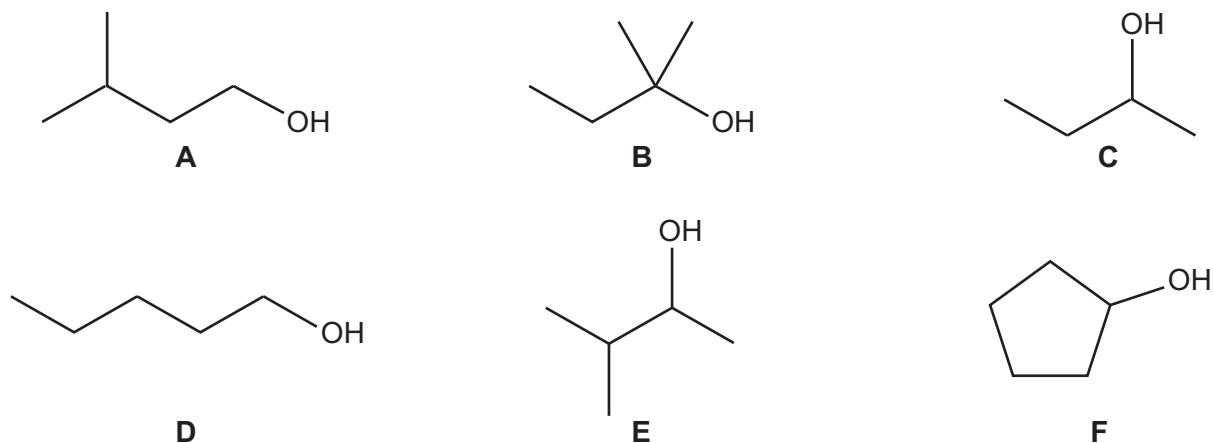
State and explain how the rates of hydrolysis of the chloroalkane and the bromoalkane would differ.

The rate of hydrolysis is slower with the chloroalkane.

The C-Cl bond is stronger than the C-Br bond (greater bond enthalpy), so more energy is needed to break the C-Cl bond.

[2]

(f)* The structures of **A–F** are repeated below.

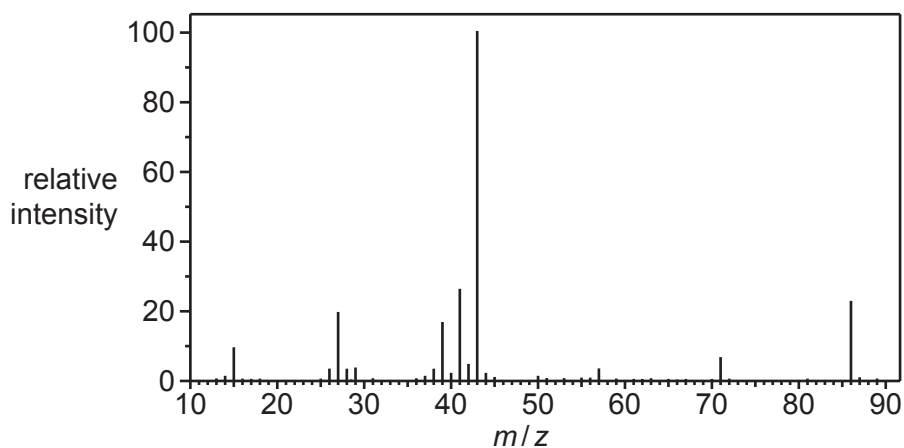


Compound **X** is one of the alcohols **A–F**.

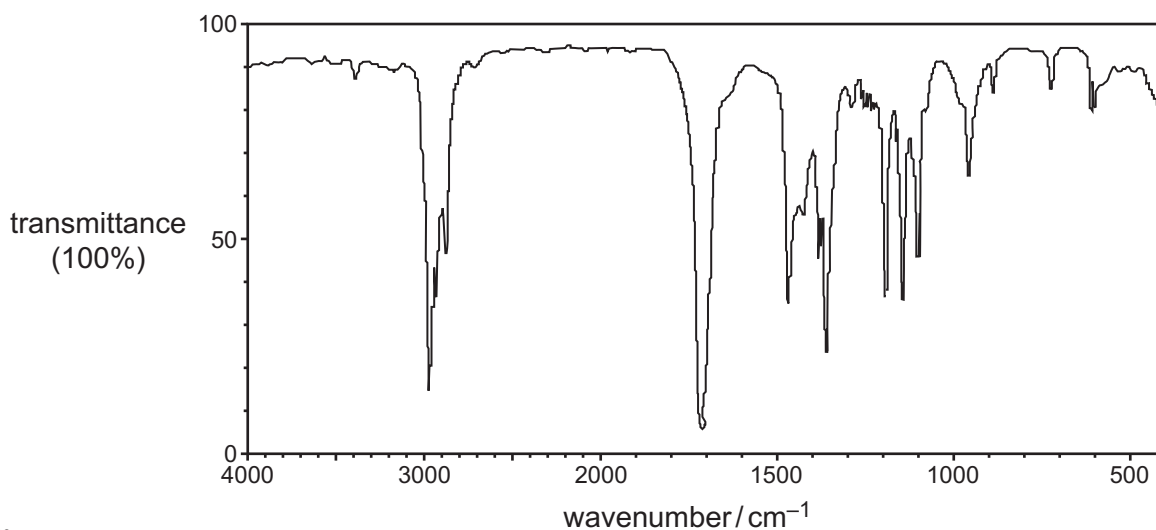
A student refluxes compound **X** with acidified potassium dichromate(VI) as an oxidising agent. A pure sample of the organic product **Y** is obtained from the resulting mixture.

The mass spectrum and IR spectrum of **Y** are shown below.

Mass spectrum of **Y**



IR spectrum of **Y**



Mass spectrum: the molecular ion (M^+) peak is at $m/z = 86$, so $M_r(Y) =$

86.0. The base peak at $m/z = 43$ is CH_3CO^+ (or C_3H_7^+).

IR: there is no broad absorption at 2500 to 3300 cm^{-1} (or 3200 to 3600 cm^{-1}), so Y has no O-H bond: it is not an alcohol or a carboxylic acid. The strong absorption at about 1700 cm^{-1} shows a C=O bond, so Y is an aldehyde or a ketone.

Refluxing a primary alcohol (A, D) with acidified $K_2Cr_2O_7$ gives a carboxylic acid (would show a broad O-H), and the tertiary alcohol B is not oxidised.

So X must be a secondary alcohol, which is oxidised to a ketone.

The secondary alcohols are C (M_r 74.0, ketone 72.0), E (M_r 88.0, ketone 86.0) and F (M_r 86.0, ketone 84.0). Only the ketone from E has $M_r = 86.0$.

So X is E, 3-methylbutan-2-ol, $(\text{CH}_3)_2\text{CHCH}(\text{OH})\text{CH}_3$, and Y is the ketone 3-methylbutan-2-one, $(\text{CH}_3)_2\text{CHCOCH}_3$. This fits $m/z = 43$ for CH_3CO^+ (or $(\text{CH}_3)_2\text{CH}^+$) and $m/z = 71$ for loss of CH_3 ($86 - 15$).

Equation: $(\text{CH}_3)_2\text{CHCH}(\text{OH})\text{CH}_3 + [\text{O}] \rightarrow (\text{CH}_3)_2\text{CHCOCH}_3 + \text{H}_2\text{O}$

Additional answer space if required

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